PB88-170527

Mathematical Model for the Fate of Hazardous Substances in Soil: Model Description and Experimental Results

(U.S.) Robert S. Kerr Environmental Research Lab
Ada, OK

1987

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1. REPORT NO. EPA/600/J-87/204	2.	3. F PB88-170527
4. TITLE AND SUBTITLE A MATHEMATICAL MODEL FOR THE FATE OF HAZARDOUS SUBSTANCES IN SOIL: Model Description and Experimental Results (Journal Version)		5. REPORT DATE 1987 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) William J. Grenney,[1] Craig L. Caupp,[1] Ronald C. Sims,[1] and Thomas E. Short[2]		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS [1]Civil and Environmental Engineering Department, Utah State University, Logan, UT 84322-4110; [2]Robert S. Kerr Environmental Research Laboratory, U.S. EPA, Ada, OK 74820		10. PROGRAM ELEMENT NO. CBWD1A 11. CONTRACT/GRANT NO. CR-810979
12. SPONSORING AGENCY NAME AND ADDRESS Robert S. Kerr Environmental Research Lab. - Ada, OK, U.S. Environmental Protection Agency, Post Office Box 1198, Ada, OK 74820		13. TYPE OF REPORT AND PERIOD COVERED Journal Article 14. SPONSORING AGENCY CODE EPA-600/15

15. SUPPLEMENTARY NOTES
Published in: HAZARDOUS WASTE & HAZARDOUS MATERIALS, Vol. 4, No. 3, pp. 223-239, Summer 1987.

16. ABSTRACT

A mathematical model was developed and implemented for evaluating fate of a hazardous substance in the unsaturated zone of soil. The model simulates vadose processes of volatilization, degradation, sorption/desorption, advection, and dispersion. Four vadose zone physical phases are considered including water, oil, soil grains, and soil-pore air. The Vadose Zone Interactive Processes (VIP) model is appropriate for use at RCRA and CERCLA sites since site-specific processes affecting transport of hazardous chemicals through the vadose zone are incorporated in the model. A RCRA land treatment system was chosen as the basis of model development. The model is implemented on IBM-PC/XT/AT compatible equipment and has an interface to accept input files from LOTUS spreadsheets. Laboratory experiments were conducted to observe transport and apparent degradation of three polynuclear aromatic hydrocarbon (PAH) compounds (anthracene, fluoranthene, and naphthalene) in sandy loam soil in separate soil columns under two flow conditions. Vadose zone concentrations of PAH compounds were evaluated as function of time (90 days) and depth (1.5 m). Experiment results were compared with the model predictions. The VIP model closely simulated fate and behavior of the three compounds through depth and time in soil columns.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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INFORMATION SERVICE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC.	19. SECURITY CLASS (This Report) UNCLASSIFIED. 20. SECURITY CLASS (This page) UNCLASSIFIED.	21. NO. OF PAGES 19 22. PRICE PC/295/A6.95 MF

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA/600/J-87/204
JOURNAL ARTICLE

HAZARDOUS WASTE & HAZARDOUS MATERIALS
Volume 4, Number 3, 1987
Mary Ann Liebert, Inc., Publishers

A Mathematical Model for the Fate of Hazardous Substances in Soil: Model Description and Experimental Results

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ABSTRACT

A mathematical model (VIP) was developed and implemented for evaluating the fate of a hazardous substance in the unsaturated zone of the soil. The model simulates vadose zone processes including volatilization, degradation, adsorption/desorption, advection, and dispersion. Four physical phases in the vadose zone are considered including water, oil, soil grains, and soil-pore air (unsaturated pore space). The Vadose Zone Interactive Processes (VIP) model is appropriate for sites under RCRA and CERCLA (Superfund) categorization since site-specific soil-waste processes affecting transport of hazardous chemicals through the vadose zone are incorporated in the model. A RCRA land treatment system was chosen as the basis of the model development. The model is implemented on IBM-PC, -XT, and -AT compatible equipment and has an interface to accept input files from LOTUS spreadsheets.

Laboratory experiments were conducted to observe the transport and apparent degradation of three polynuclear aromatic hydrocarbon (PAH) compounds (anthracene, fluoranthene, and naphthalene) in sandy loam soil in separate soil columns under two flow conditions. Vadose zone concentrations of the PAH compounds were evaluated as function of time (90 days) and depth (1.5 m). Results of the experiments were compared with the model predictions.

The VIP model closely simulated the fate and behavior of the three compounds through depth and through time in the vadose zone conditions in the soil columns. It was possible to use literature values for partition coefficients, apparent degradation rates, and interpore water velocity in the model for all three compounds.

INTRODUCTION

Hazardous waste land treatment (HWLT) is a technology that utilizes the in situ, or assimilative, capacity of the soil to achieve treatment and ultimate disposal while protecting public health and the environment. HWLT is defined as the technology pertaining to application/incorporation of waste into the upper layers of the soil to degrade, transform, and/or immobilize hazardous chemicals contained in an applied waste (40 Code of Federal Regulations (CFR) Part 264).

A microcomputer model named VIP (Vadose Zone Interactive Processes) was developed at Utah State University to provide a mathematical description of a land treatment system. Based upon conceptual models of the land treatment processes, VIP incorporates specific requirements for land treatment demonstrations specified by the U.S. Environmental Protection Agency (EPA) in 40 CFR Part 264.272 and provides a framework for integrating and evaluating relevant information including: (1) evaluation of literature and/or experimental data for the selection of constituents most difficult to treat, considering the combined effects of degradation and immobilization (principal hazardous constitutes, PHCs), (2) evaluation of the effects of site characteristics on treatment performance (soil type, soil permeability), (3) determination of the effects of design and operating parameters (loading rate, etc.) on treatment performance, (4) evaluation of the effects of environmental parameters (season, infiltration rate), and (5) comparison of the effectiveness of treatment using different design and management practices to maximize treatment.

The VIP model extends previous work by Short [1], to take into account more site specific parameters. These include application rate and application frequency, site temperature, degradation and soil-water partition coefficients for chemicals as a function of soil depth. Initial chemical concentrations above background levels at previously contaminated sites or at well-managed sites that have a history of waste application can also be accommodated. The VIP model is appropriate for sites under RCRA and CERCLA (Superfund) categorization since site-specific soil-waste processes affecting transport of hazardous chemicals through the vadose zone are incorporated in the model. Results of VIP model evaluation allow ranking of chemical constituents with respect to potential transport, and identification of management techniques based on controlling either migration or controlling degradation or both [2].

Laboratory experiments were conducted to observe the sorption and degradation processes for three polynuclear aromatic hydrocarbon (PAH) compounds in soil-water systems. Results of the experiments were compared with model predictions.

MODEL DESCRIPTION

The model describes the fate of a hazardous organic substance in the soil. For a land treatment system, the soil column is considered to be made up of two zones: the zone of incorporation (ZOI) and the lower treatment zone (LTZ). The ZOI (also called the plow zone) is the top layer in which the substance is mixed during application. It is typically about 15 cm deep. The LTZ extends below the ZOI to a depth of about 1.5 m and contains substances which have been mobilized and transported downward from the ZOI.

The term "constituent" refers to the hazardous substance being tracked by the model. A constituent exhibits homogeneous chemical properties, i.e., its environmental characteristics may be quantified by a specific isotherm or degradation rate. A constituent may be a pure compound or it may be a mixture of several compounds as long as the behavior of the mixture can be adequately described by composite constituent parameters.

A "phase" is defined as a physical component of the soil environment in which the constituent moves. In this model, the following phases are defined: soil grains, pore water, pore oil, and pore air (unsaturated pore space). The relative amounts of the phases may change with time and depth in the soil.

The fate of a constituent in the soil column depends on mobilization, volatilization, and decomposition rate.

Mobilization

Once applied to the land and mixed into the ZOI, a constituent may be mobilized by three mechanisms: advection, dispersion, and migration between/among phases. Equation (1) describes these mechanisms mathematically for one phase in a control volume slice (thickness = dz) of a one-dimensional (vertical) soil column.

$$\frac{\partial C\Theta A dz}{\partial t} = \frac{\partial \Theta A D \frac{\partial C}{\partial z}}{\partial z} dz + \frac{\partial(-V\Theta AC)}{\partial z} dz + \psi A dz - \mu C\Theta A dz \qquad (1)$$

where:

A = horizontal area of the control volume, (m^2)
C = concentration of the constituent in the water phase (g/m^3)
D = dispersion coefficient for the phase, (m^2/day)
dz = depth of control volume, (m)
t = time, (days)
V = vertical pore velocity of the phase, (m/day)
z = depth, positive downwards (m)
Θ = volume of the phase within the control volume, (m^3 phase/m^3 control volume)
ρ = bulk density of the soil (g-soil/m^3 control volume)
μ = first order decay rate for the constituent within the phase, (1/day)
ψ = mass adsorption rate into the phase from other phases, (g/m^2/day/m^3 control volume)

Advection and dispersion. Mobilization by the advection and dispersion of the phase within the soil column is represented by the first two terms on the right-hand-side of Equation (1). Both of these mechanisms may be significant for the water and air phases. Although in some applications they may also be significant for the oil phase, this version of the model constrains the oil to the ZOI. Laboratory experiments on mobility of the oil phase in soil are currently underway at Utah State University (USU). The soil grain phase is immobile.

Dispersion in the water phase has been inactivated in this version of the model because the nonequilibrium adsorption/desorption process (described later) provided dispersive phenomena sufficient to simulate observed data. However, if and when activated, it will be solved by a scheme similar to that for air.

Adsorption/desorption. The third term on the right-hand-side of Equation (1) represents migration of the constituent between/among phases. This mass flux of the constituents among phases is modeled as a sorption mechanism. Enfield [3] and Lapidus and Amundson [4] have expressed the sorption mechanism as a linear gradient process of the following form:

$$\psi = -\kappa\, \Theta_2\, (K_{2,1}\, C_1 - C_2) \qquad (2)$$

where the numerical subscripts distinguish the two phases, and:

κ = a mass transfer rate coefficient (1/day)
$K_{2,1}$ = the linear partition coefficient for phase 2 with respect to phase 1 [g/m^3 phase 2)/(g/m^3 phase 1)] or [(g/g soil)/(g/m^3 phase 1)].

In general sorption can occur directly between any two phases that are in contact, and Equation (2) could be expanded to describe mass flux among more than two phases at a time. However, estimating meaningful values for the additional coefficients would be extremely difficult, and so it is assumed that constituent migration from one phase to another must pass through the water phase. Consequently, Equation (2) is applied between the water phase and each of the other phases [1,3]

Volatilization. Volatilization is represented in the model by two processes: mass flux into the air phase and advection/dispersion. The mass flux of the constituent into the air phase is modeled by Equation (2). The constituent is then transported with the air phase by advection and dispersion, depending on the boundary conditions at the soil surface.

Degradation

The fourth term of Equation (1) represents the degradation (biochemical, photochemical or hydrolysis). Apparent degradation refers to the measurement of the loss of a constituent from the soil matrix without regard to mechanism and may

include a volatilization component for volatile chemicals. First-order kinetics are generally assumed. Field and laboratory studies of other investigators, Sims, et al. [5] and Sims and Overcash [6], have indicated that the use of first order kinetics provides a reasonable approximation for the degradation of many hazardous substances in soil systems. Because the constituent may degrade at different rates in different phases, separate coefficients (μ) are provided for each phase in the model. The apparent degradation rate coefficients are permitted to vary with depth in the model.

MODEL EQUATIONS

Based on the preceding discussion, Equation (1) can be applied to the four phases in a homogeneous soil column of unit cross-sectional area as follows:

$$\frac{\partial C_w}{\partial t} = -V_w \frac{\partial C_w}{\partial z} - \mu_w C_w \tag{3a}$$

$$- \frac{\kappa}{\theta_w} (\theta_a K_{aw} + \theta_o K_{ow} + \rho K_{sw}) C_w$$

$$+ \frac{\kappa}{\theta_w} (\theta_a C_a + \theta_o C_o + \rho C_s)$$

$$\frac{\partial C_a}{\partial t} = -V_a \frac{\partial C_a}{\partial z} + D_a \frac{\partial^2 C_a}{\partial z^2} - \mu_a C_a \tag{3b}$$

$$+ \kappa (K_{aw} C_w - C_a) - C_a \frac{\partial \theta_a}{\partial t}$$

$$\frac{\partial C_o}{\partial t} = -\mu_o C_o + \kappa (K_{ow} C_w - C_o) - C_o \frac{\partial \theta_o}{\partial t} \tag{3c}$$

$$\frac{\partial C_s}{\partial t} = -\mu_s C_s + \kappa (K_{sw} C_w - C_s) \tag{3d}$$

$$\frac{\partial \theta_o}{\partial t} = -\gamma_o \theta_o \tag{3e}$$

$$\theta_a = \phi - \theta_w - \theta_o \tag{3f}$$

where the subscripts w, a, o and s indicate the water, air, oil and soil grain phases respectively; K_{aw}, K_{ow} and K_{sw} are linear partition coefficients; and ϕ is soil porosity; ρ is soil bulk density; and γ_o is the degradation rate of the oil phase.

Velocity of the water phase

V_w in Equation (3a) is the pore velocity of the water phase. The value for V_w is calculated in the model by dividing the average infiltration rate (V') by the water content of the soil (θ_w). The water content is estimated from the soil properties by the procedure of Clapp and Hornberger [7]:

$$\theta_w = \phi \left[\frac{V'}{c}\right]^{\frac{1}{2b+3}} \tag{4}$$

where V' is the recharge rate in (cm/min), c is the saturated hydraulic conductivity (cm/min), and b is a coefficient dependent on soil properties.

SOLUTION ALGORITHMS

The model Equations (3a) - (3f) are programmed in FORTRAN and solved numerically. The program will run on IBM-PC, -XT, and -AT compatible equipment, and has a built-in editor or accepts input files from LOTUS spreadsheets. An option for graphical output is provided.

The computer code is designed in a modular structure to provide for convenient enhancement in the future. The modular structure also provides a convenient means for evaluating the behavior of various processes by isolating the modules for independent analysis. The main solution algorithm is divided into four functional modules: loading rates, degradation, phase transport, and sorption.

Loading rates

The user specifies the initial constituent concentration profile in the soil column and the frequency of waste application. Each waste application is assumed to be instantaneously and uniformly incorporated into the ZOI. This is accomplished by establishing a new initial condition to account for the additional mass in the ZOI each time waste is applied.

Degradation

This module solves the degradation terms of Equations (3a) - (3f) for the constituents in each phase and for the oil phase itself. The concentration of a constituent remaining in the water and soil phases at the end of a finite time interval (Δt) is calculated by:

$$C_{(t+\Delta t)} = C_{(t)}\, e^{-\mu \Delta t} \tag{5}$$

The changes in the volume of the oil and air phases are calculated by:

$$\theta_{o(t+\Delta t)} = \theta_{o(t)}\, e^{-\gamma_o \Delta t} \tag{6a}$$

$$\theta_{a(t+\Delta t)} = \phi - \theta_w - \theta_{o(t+\Delta t)} \tag{6b}$$

and the concentrations in the oil and air phases are calculated by:

$$C_{o(t+\Delta t)} = \frac{\theta_{o(t)}}{\theta_{o(t+\Delta t)}} C_{o(t)}\, e^{-\mu_o \Delta t} = C_{o(t)}\, e^{(\gamma_o - \mu_o)\Delta t} \tag{7a}$$

$$Ca_{(t+\Delta t)} = \frac{\theta_{a(t)}}{\theta_{a(t+\Delta t)}} C_{a(t)} e^{-\mu_a \Delta t} \tag{7b}$$

Phase transport

The constituent is transported by the advection of the water phase and by the advection and dispersion of the air phase. The advective transport of the water phase is formulated as an explicit, upstream difference [8] as follows:

$$C_{(i,t+\Delta t)} = C_{(i,t)} + \frac{\hat{V}\Delta Z}{\Delta t} \left(C_{(i-1,t)} - C_{(i,t)}\right) \tag{8a}$$

where $\hat{V}$ is an adjusted velocity and Δt is calculated such that:

$$\frac{\hat{V}\Delta Z}{\Delta t} = 1 \tag{8b}$$

This formulation provides an exact solution for the advective water transport and will preserve a vertical concentration gradient at the leading edge of the transport wave. The parameter V is obtained by adjusting the pore velocity of the water, V, to account for the retardation caused by adsorption as described later.

Experience has been gained over the years concerning the behavior of numerical solutions for the advection and dispersion of water quality constituents. The advection and dispersion terms have been solved successfully for steady and unsteady flow by explicit technique [8,9,10] and implicit technique [10,11,12,13,14]. The advection and dispersion terms of the air phase are formulated as an implicit difference equation:

$$C_{(i,t)} = A_1 C_{(i-1,t+\Delta t)} + A_2 C_{(i,t+\Delta t)} + A_3 C_{(i+1,t+\Delta t)} \qquad (9)$$

$$A_1 = -\frac{D_a \Delta t}{\Delta z^2} + \frac{V_a \Delta t}{\Delta z}$$

$$A_2 = 1 + \frac{2D_a \Delta t}{\Delta z^2} - \frac{V_a \Delta t}{\Delta z}$$

$$A_3 = -\frac{D_a \Delta t}{\Delta z^2}$$

The system of Equations (9) is expressed in matrix form and solved by numerical techniques.

Adsorption/desorption

Two options were evaluated for representing the adsorption/desorption mechanisms in the model. The first method assumes local equilibrium [1,3,4] and requires that the concentrations be in equilibrium in all phases at the end of each time step (Δt). This may be accomplished by the following calculations:

$$M_{(i)} = C_{w(i)}\theta_{w(i)} + C_{s(i)}\rho_{(i)} + C_{o(i)}\theta_{o(i)} + C_{a(i)}\theta_{a(i)} \qquad (10)$$

$$B_{w(i)} = \theta_{w(i)} + \theta_{o(i)}K_{ow(i)} + \theta_{a(i)}K_{aw(i)} + \rho_{(i)}K_{sw(i)}$$

$$C_{w(i)} = M_{(i)}/B_{w(i)}$$

$$C_{a(i)} = K_{aw(i)}C_{w(i)}$$

$$C_{o(i)} = K_{ow(i)}C_{w(i)}$$

$$C_{s(i)} = K_{sw(i)}C_{w(i)}$$

where all time dependent variables are measured at time $t + \Delta t$, $M_{(i)}$ is the total mass in the control volume (i), and B_w is the local equilibrium coefficient for the control volume. These equations preserve the mass balance of the constituent and impose the local equilibrium assumption.

The second method involves solving the kinematic terms (Equation 2) in each of the Equations (3a) - (3d). This is accomplished by expressing them as implicit difference equations across the time increment (Δt). For each control volume (i):

$$\frac{C_{w(t+\Delta t)} - C_{w(t)}}{\Delta t} = \frac{-\kappa\theta_o}{\theta_w}\left[K_{ow}C_{w(t+\Delta t)} - C_{o(t+\Delta t)}\right]$$

$$\frac{-\kappa\theta_a}{\theta_w}\left[K_{aw}C_{w(t+\Delta t)} - C_{a(t+\Delta t)}\right]$$

$$\frac{-\kappa\rho}{\theta_w}\left[K_{sw}C_{w(t+\Delta t)} - C_{s(t+\Delta t)}\right] \qquad (11a)$$

$$\frac{C_{o(t+\Delta t)} - C_{o(t)}}{\Delta t} = \kappa\left[K_{ow}C_{w(t+\Delta t)} - C_{o(t+\Delta t)}\right] \qquad (11b)$$

and the equations for air and soil are identical in form to Equation (11b). These equations are rearranged and solved by a one-pass matrix reduction procedure. The system of equations and the numerical method preserve the mass balance across the time increment.

This second option was incorporated into the VIP model. Nonequilibrium adsorption/desorption kinetics were chosen when a numerical algorithm was developed which converged to the local equilibrium assumption for large values of kappa (κ).

NUMERICAL SOLUTION

Modular approach

There are three important benefits to programming numerical techniques in functional modules. First, the program is easy to modify and upgrade. Second, more than one solution procedure can be used, thereby allowing the use of a specific technique (closed-form, explicit, implicit) best suited for the equations in each module. Third, the behavior of the various physical and biochemical mechanisms being represented may be evaluated by isolating the modules for independent analysis. These features also enhance the use of the model as a research tool because a variety of hypotheses, expressed as mathematical equations, may be conveniently inserted and tested.

Nonequilibrium adsorption/desorption

An algorithm was developed specifically to solve the system of differential equations containing nonequilibrium adsorption/desorption [15]. The performance of the algorithms may be best described by considering the systems of Equations (3a) - (3f) applied to a two-phase (water and soil) environment without dispersion or decay.

$$\frac{\partial C_w}{\partial t} = -V_w \frac{\partial C_w}{\partial z} - \frac{\kappa\rho}{\theta_w}\left(K_{sw}C_w - C_s\right) \qquad (12a)$$

$$\frac{\partial C_s}{\partial t} = \kappa\left(K_{sw}C_w - C_s\right) \qquad (12b)$$

The exact solutions for Equations (12a) and (12b) were obtained [15] and applied using the coefficient values for naphthalene shown later in Table 2 (except with decay equal to zero). An initial concentration of 5.21 micrograms/gram soil was placed in the plow zone. The initial concentration in the water was zero. Figures 1a and 1b show the concentration distribution in the water and the soil after 90 days, for six values of kappa (κ) ranging from 0.01 to 1000 per day day. At very high adsorption/desorption rates, (κ = 1000) the initial distributions in the plow zone is advected at the retarded velocity:

$$\hat{V} = V/\left(1 + \frac{\rho K_{sw}}{\theta_w}\right) \qquad (13)$$

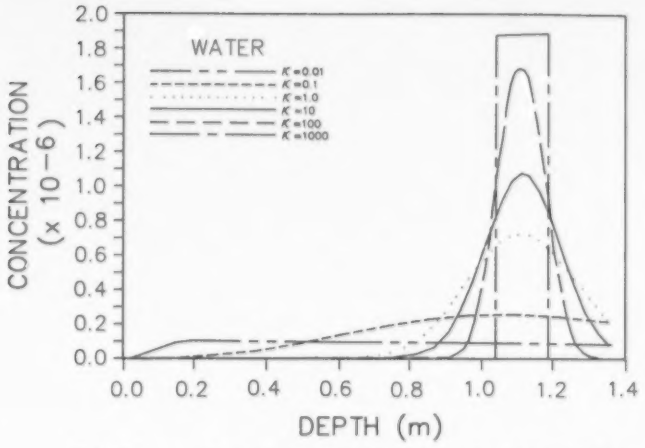

FIGURE 1A. EXACT SOLUTION FOR NONEQUILIBRIUM ADSORPTION / DESORPTION AFTER 90 DAYS.

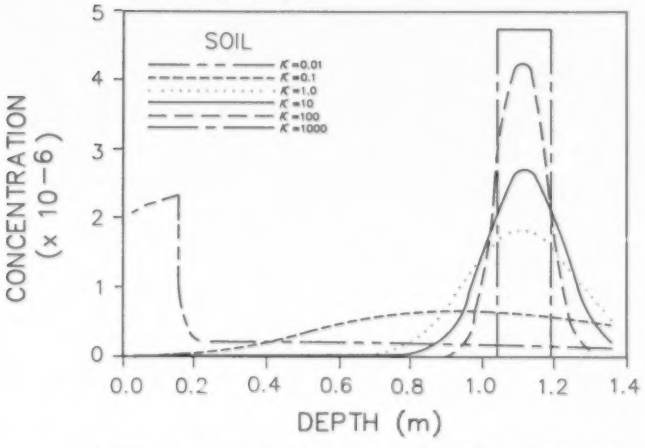

FIGURE 1B. EXACT SOLUTION FOR NONEQUILIBRIUM ADSORPTION / DESORPTION AFTER 90 DAYS.

and conforms to the exact solution based on the assumption of local equilibrium [1]. As kappa decreases, the dispersion of the distribution increases. At very low values of kappa, the mass transfer rate between phases is so slow that almost all of the constituent remains on the soil in the plow zone.

The numerical solution using the VIP model with $\Delta Z = 0.015$ m was within 2 percent of the exact solution, and the plots could not be visibly distinguished from Figures 1a and 1b. Thus, the numerical solution in the VIP model accurately represented the two extremes of nonequilibrium adsorption/desorption kinetics ($\kappa \rightarrow 0$ and $\kappa \rightarrow \infty$) as well as intermediate results. Sensitivity analysis indicated that when $\Delta Z = 0.015$ m the VIP solution agreed with the exact solution for a wide range of coefficient values [15]. When ΔZ was increased to 0.025 m, differences between the solution peaks of as much as 20 percent were observed.

Data presented by other investigators [16,17,18] shows the dispersive tendency exhibited in Figures 1a and 1b. The experience of the authors, after reviewing those data and working with the model and the data in this study, led to the

selection of a value for kappa (κ) of 1.0 per day as a reasonable approximation of the dispersive phenomenon associated with the adsorption/desorption mechanism. When kappa was large (local equilibrium) the resulting distribution was much too peaked (or rectangular) to be realistic. When kappa was significantly less than 1.0, the distribution was much too dispersed. A value for kappa of 1.0 was used consistently in this study for model comparisons with laboratory data.

Sequence of calculations

Each of the four program modules was run independently and the model responses were compared to closed form solutions. Pure advection in the water phase was simulated by imposing an initial concentration in the plow zone water and setting kappa very low (κ = 0.01). The result was plug flow traveling at the pore velocity of the water as expected.

Running the model with only degradation produced exponential decay of the initial concentrations as expected. Running the sorption module with a very high value for kappa (κ = 1000) and the degradation module produced exponential decay in each phase associated with equilibrium among phases at the end of each time increment. Running the decay, advection, and sorption modules simultaneously produced the expected results of a decaying slug of constituent being transported at the average pore velocity of the water and in equilibrium with the soil at the end of each time increment. The decay rates and the mass balance (accounting for decay) maintained accuracy to three significant figures for a one-year simulation.

LABORATORY DATA

Laboratory experiments were conducted to observe the fate of three polynuclear aromatic hydrocarbon (PAH) compounds in soil columns under two flow conditions; moderate and high flow rates.

Experimental Conditions

Six KIMAX glass columns, each 4 inches in diameter and 5 feet long, were filled with sandy loam soil, with an organic carbon content of 0.39 percent. The soil had been excavated from the top six inch layer at a site in Southern Uintah County, Utah.

A PAH compound was thoroughly mixed into the top 15 cm of each soil column as shown in Table 1. The columns were located in a constant temperature room at 18 $\pm$ 1°C and were covered to prevent photodecomposition of the PAH compounds. The experiments were operated continuously for 3 months.

TABLE 1

Summary of the experimental conditions.

PNA applied	Average Flow cm/day	Initial load micro-gram/gram-dry soil
Anthracene	2.90	1.61
Anthracene	0.95	1.61
Fluoranthene	3.14	1.61
Fluoranthene	0.56	1.61
Naphthalene	4.30	5.21
Naphthalene	0.95	5.21

Tap water was applied to the top of each column at constant rates by means of

constant head siphons. Infiltration rates are shown in Table 1. The moderate flow rates of 0.56 and 0.95 cm/day produced unsaturated flow. Relatively high flow rates of 2.90, 3.14, and 4.30 cm/day were also evaluated.

Sampling Procedure

During the experiments leachate samples were collected and analyzed for the PAH compounds. At the termination of the experiments, soil samples were collected from each column at various depths and analyzed for PAH soil concentrations. Samples were tested using U.S. EPA guidelines for test methods for PAH compounds [19,20].

RESULTS

The model was run for each of the experimental conditions using literature values for partition coefficients, apparent decay rates, and interpore water velocity. These model results were then compared to the laboratory results to test the ability of the model to simulate the mobility and apparent degradation of selected compounds in a two phase system (soil/water) using literature values for the model coefficients.

Table 2 summarizes values for compound specific model coefficients used in this study. The values for soil-waterr partition coefficients were calculated by the formula published by Schwarzenbach and Westall [21]. The values for the decay rates were estimated by comparing the mass remaining after 90 days to the initial mass for the columns with the high flow rates. These rates fall within the ranges reported by Sims and Overcash [6]. The apparent degradation rates have been demonstrated by Park [22] to represent a biodegradation process for anthracene and fluoranthene. For naphthalene, however, volatilization may account for as much as one-third of the "apparent" degradation [22]. Only apparent degradation literature values were used for these experiments.

TABLE 2

Coefficient Values Used in Model Runs.

	FLOW CC/DAY/M^2	INITIAL LOAD MICROGRAM/ GRAM-SOIL	K_{SW} ((G-PAH/G-SOIL)/ (G-PAH/M^3-WATER	DECAY RATE 1/DAY	RANGE DECAY RATE 1/DAY
ANTHRACENE					
High	2.90	1.61	19.3E-6	0.0060	0.004-0.21
Moderate	0.95	1.61	19.3E-6	0.0060	
Moderate	0.95	1.61	19.3E-6	0.0120	
FLUORANTHENE					
High	3.14	1.61	82.9E-6	0.0040	0.004-0.016
Moderate	0.56	1.61	82.9E-6	0.0040	
NAPHTHALENE					
High	4.30	5.21	3.16E-6	0.0147	0.005-5.78
Moderate	0.95	5.21	3.16E-6	0.1	

Anthracene Moderate Flow

Figure 2 shows laboratory results for anthracene under moderate flow conditions and the predicted soil concentration profile after 90 days. The laboratory data indicate that anthracene is non-mobile and decays to 34 percent of the initial concentration after 90 days. Use of the literature value for the soil-water

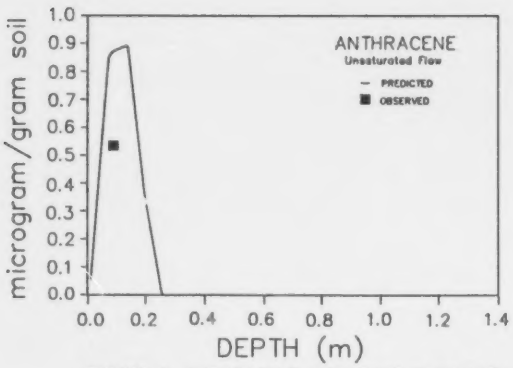

FIGURE 2. ANTHRACENE MODERATE FLOW WITH MODERATE DECAY RATE.

partition coefficient in the model resulted in an accurate estimation of the mobility of anthracene. However, the measured apparent decay was twice as rapid as the apparent decay at high flow of 0.006 1/day. When the apparent decay rate in the model was doubled to 0.012 1/day, the predicted profile and experimental profile match very well (as shown in Figure 3). The calibrated apparent decay rate of 0.012 1/day is well within the range of reported values 0.004-0.21 1/day [6]. The depth-concentration profiles for both the laboratory data and model simulation indicated that anthracene would not migrate more than a few centimeters from the 15 cm plow zone after 90 days.

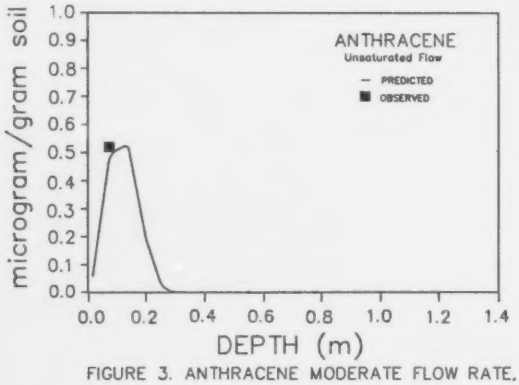

FIGURE 3. ANTHRACENE MODERATE FLOW RATE.

Anthracene High Flow

Figure 4 shows that the use of the literature value for the partition coefficient results in accurate estimates of the mobility of anthracene under high flow conditions. Comparison of the moderate and high flow experiments indicates that the apparent decay rate is less for the high flow experiment. Both the experimental and the model results showed anthracene being advected below the zone of incorporation to about 25 cm.

Fluoranthene Moderate Flow

Figure 5 presents the laboratory data and model predictions for fluoranthene at moderate flow conditions. Results from the model, using the literature value for the soil-water partition coefficient and the estimated apparent decay, matche

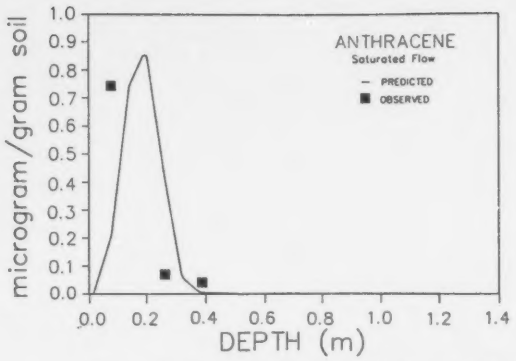

FIGURE 4. ANTHRACENE HIGH FLOW RATE WITH MODERATE DECAY RATE.

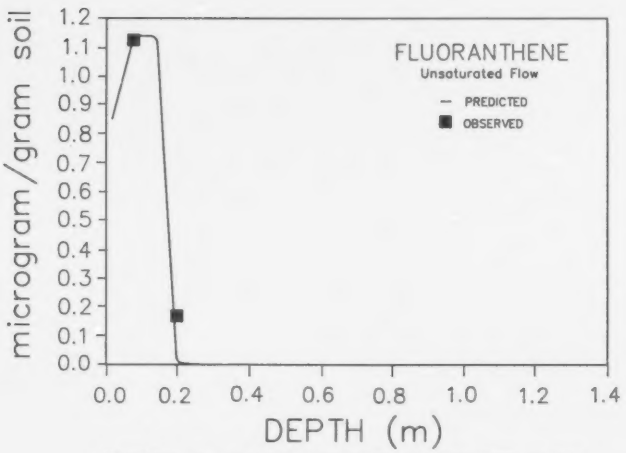

FIGURE 5. FLUORANTHENE MODERATE FLOW.

the laboratory results. Fluoranthene is non-mobile and has an apparent degradation rate of approximately 0.004 1/day.

Fluoranthene High Flow

Figure 6 presents the laboratory data and model predictions for fluoranthene under high flow conditions. Like fluoranthene under moderate flow conditions, there is very good agreement between simulated and observed soil concentration values. The increased flow rate was not accompanied by a reduction in the apparent decay rate or an increase in the mobility of fluoranthene in the laboratory column.

Naphthalene Moderate Flow

Naphthalene decayed rapidly under the moderate flow regime and had completely disappeared from the column soil at the end of 90 days. Using the literature values given in Table 2, the model simulated the same result.

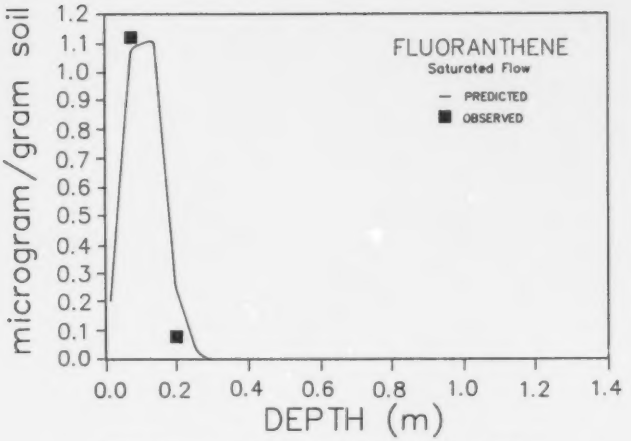

FIGURE 6. FLUORANTHENE HIGH FLOW.

Naphthalene High Flow

Figures 7 and 8 show the laboratory data and model predictions for naphthalene under high flow conditions. Naphthalene was advected downward in the column with the peak reaching a depth of approximately 1.2 meters in 90 days as shown in Figures 7 and 8. Using the literature values for the soil-water partition coefficient (Table 2), the model predicted a peak concentration reasonably well. Figure 7 shows the model predictions at 30 day intervals and demonstrates the advective transport as well as the dispersive action caused by nonequilibrium adsorption/desorption with kappa (κ) equal to 1.0. Figure 8 shows the model predictions at 90 days for three values of kappa. For high values of kappa (local equilibrium assumption) the predicted distribution has advected about the proper distance. However, it is too rectangular in shape to agree with the observed data. For low values of kappa (κ = 0.1), the model prediction is too dispersed. For kappa equal to 1.0, the predicted distribution is most accurate.

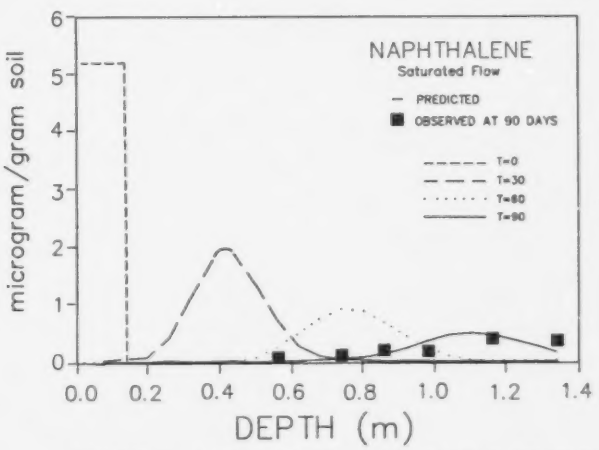

FIGURE 7. NAPHTHALENE HIGH FLOW RATE WITH MODEL OUTPUT EVERY 30 DAYS.

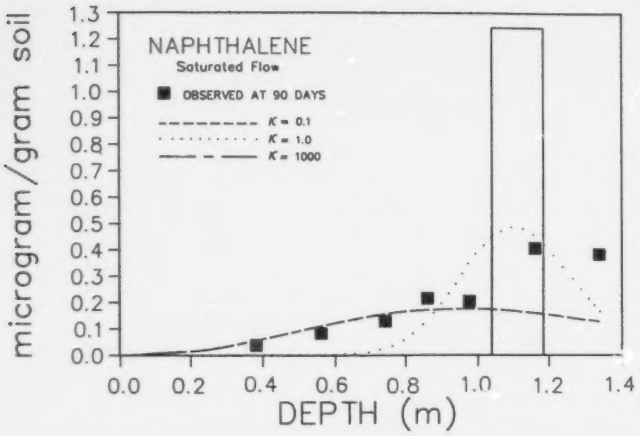

FIGURE 8. NAPHTHALENE HIGH FLOW RATE SHOWING THE EFFECT OF KAPPA(κ) ON MODEL PREDICTIONS.

DISCUSSION

The model adequately simulated the mobility and apparent decay of anthracene, fluoranthene, and naphthalene in laboratory soil columns. Literature values [21] were used for the partition coefficients in the model simulations of the experiments. Apparent decay rates were estimated from the mass remaining in the columns operated at high flow conditions. These rates were near the lower end of the ranges reported by Sims and Overcash [6]. The high flow rates appeared to create conditions unfavorable for the apparent decay of naphthalene and anthracene. It was hypothesized that the higher recharge rates might possibly reduce or limit the diffusion of oxygen into the soil or volatilization in the case of naphthalene, causing a reduction in apparent degradation rates.

Compared to moderate flow rates, results at high flow rates indicated that the apparent decay rates were reduced by a factor of 10 for naphthalene, a factor of 2 for anthracene, and no reduction for fluoranthene. The effect of flow rate on decay rate parallels the relative molecular weights of the substances. Naphthalene has the lowest molecular weight and has the widest variation of reported decay rates (Table 2). Since the apparent decay rate of naphthalene is the fastest of the three compounds, it is reasonable to assume that less than favorable environmental conditions could have a large effect on the apparent decay rate of naphthalene. Anthracene has a molecular weight between naphthalene and fluoranthene and the magnitude of variation in reported apparent decay rates for anthracene is smaller than the magnitude of variation for naphthalene and larger than that for fluoranthene. Fluoranthene has the largest molecular weight and has the narrowest range of reported apparent decay rates. In contrast to naphthalene and anthracene, there was no obvious difference in apparent decay rates between high and moderate flow in the experiments with fluoranthene.

SUMMARY AND CONCLUSIONS

A mathematical model (VIP) was developed and implemented for evaluating the fate of a hazardous substance in four physical phases of the soil environment: water, oil, soil grains, and pore air (unsaturated pore space). The model includes the following mechanisms: volatilization, degradation, adsorption/desorption, advection, and dispersion. The model is implemented on IBM-PC, -XT, and -AT compatible equipment, and has a built-in editor and accepts input files from LOTUS spreadsheets.

The program was structured in four functional modules and the modules were tested independently and together. The model was found to be numerically stable, maintain a mass balance for the constituent, and agree closely with known results for analytical test problems in the range of practical applications. Because of its modular structure, the program was found to be an effective research tool. A variety of hypotheses, expressed as mathematical equations, may be conveniently inserted and tested in the model.

Laboratory experiments were conducted to observe the transport and degradation of three polynuclear aromatic hydrocarbon (PAH) compounds in soil columns under two flow conditions.

The model closely simulated the fate and behavior of three polynuclear aromatic hydrocarbon (PAH) compounds in a sandy loam soil during a three month period. Degradation and immobilization were significant processes affecting the behavior of the PAH constituents in the sandy loam soil. The model was accurate at both moderate and high infiltration rates.

It was possible to use literature values for the soil-water partition coefficients in the model simulations for all three PAH compounds. However, apparent decay rates were observed to vary significantly with flow rate. At high flow rates, the values of the apparent decay rates were at the lower end of the range of values reported in the literature [6].

High recharge rates may reduce or limit the diffusion of oxygen into the soil as saturated conditions are approached. Reduction in the decay rate of easily degradable constituents may result, as well as mobilization of constituents with low soil partition coefficients. This was observed for naphthalene, where the decay rate was an order of magnitude lower for high than for moderate flow. The decay rate of anthracene, with a larger molecular weight than naphthalene and a lower decay rate, was reduced by a factor of two under high infiltration conditions. Fluoranthene, with the largest molecular weight and partition coefficient and lowest decay rate, was unaffected at high infiltration conditions.

The VIP model application using literature and/or laboratory results provides an approach and a methodology for predicting the behavior of hazardous constituents in soil systems, and for addressing requirements of the U.S. EPA concerning land treatment demonstrations as specified in the Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations [23].

ACKNOWLEDGMENTS

This work was sponsored by the U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, under Cooperative Agreement number CR-813211-01. John E. Matthews was the project officer. This work has not been subject to the agency's peer review, and therefore, does not necessarily reflect the views of the agency.

Support was also provided by the Civil and Environmental Engineering Department and the Vice President for Research at Utah State University.

REFERENCES

1. Short, T.E., "Modeling of Processes in the Unsaturated Zone," In Land Treatment: A Hazardous Waste Management Alternative, R.C. Loehr and J.F. Malina, Jr. (Eds.) Water Resources Symposium No. 13, Center for Research in Water Resources, The University of Texas, Austin, TX, 1986, 211-240.

2. Sims, R.C., et al., "Review of In-place Treatment Techniques for Surface-Contaminated Soils," U.S. Environmental Protection Agency, Cincinnati, Ohio, Volumes 1 & 2, EPA-540/2-84-003a,b (1984).

3. Enfield, C.G., D.M. Walters, J.T. Wilson, and M.D. Piwoni, "Behavior of Organic Pollutants During Rapid-Infiltration of Wastewater into Soil: II Mathematical Description of Transport and Transportation," Hazardous Waste and Hazardous Materials, 3:(1):57-76 (1986).

4. Lapidus, L., and Amundson, N.R., "Mathematics of Adsorption in Beds. VI. The Effects of Longitudinal Diffusion in Ion Exchange and Chromatographic Columns," Journal of Physical Chemistry, 56:984-988, (1952).

5. Sims, R.C., J.L. McLean, W.J. Doucette, R.R. Dupont, J.L. Sims, "Land Treatment Potential for U.S. EPA Listed Hazardous Wastes," Cooperative Agreement No. CR-813211 between the United State Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, and Utah State University, (in press).

6. Sims, R.C. and M.R. Overcash, "Fate of Polynuclear Aromatic Compounds (PNAs) in Soil-Plant Systems," Residue Reviews, 88:1-68 (1983).

7. Clapp, R.B. and G. Hornberger, "Empirical Equations for Some Soil Hydraulic Properties," Water Resources Research 14:601-604 (1978).

8. Bella, D.A. and W.J. Grenney, "Finite-difference Convection Errors," Journal of the Sanitary Engineering Division, 96(SA6):1361-1375 (1970).

9. Holley, E.R., Jr. and D.R.F. Harleman, Dispersion of Pollutants in Estuary Type Flows, Hydrodynamics Laboratory, Report No. 74. MIT, Cambridge 39, Massachusetts, 1965, 191 p.

10. Hann, R.W., Jr., and P.J. Young, Mathematical Models of Water Quality Parameters for Rivers and Estuaries, Texas Water Resources Institute Report TR-45. Texas A & M University, 1972, 424 p.

11. Harleman, D.R.F., C.H. Lee, and L.C. Hall, "Numerical Studies of Unsteady Dispersion in Estuaries," Journal of the Sanitary Engineering Division, 94:(SA5)897-911 (1968).

12. O'Connor, D.J., J.P. St. John, and D.M. DiToro, "Water Quality Analysis of the Deleware River Estuary," Journal of the Sanitary Engineering Division, 94:(SA6)1225-1252 (1968).

13. Prych, E.A., and T.R.E. Chidley, "Discussion on Numerical Studies of Unsteady Dispersion in Estuaries," Journal of the Sanitary Engineering Division, 95:(SA5)959-967 (1969).

14. Grenney, W.J., M.C. Teuscher, and L.S. Dixon, "Characteristics of the Solution Algorithms for the QUAL II River Model," Journal of the Water Pollution Control Federation, 50(1):151-157 (1978).

15. Grenney, W.J., C.L. Caupp, and R.C. Thompson, Dispersion in the Vadose Zone Due to Nonequilibrium Adsorption Kinetics, Department of Civil and Environmental Engineering, Utah State University, Logan, Utah 84322 (in preparation).

16. Enfield, C.G., R.F. Carsel, S.Z. Cohen, T. Phan, and D.M. Walters, "Approximating Pollutant Transport in Ground Water," Groundwater, 20:(6)711-722 (1982).

17. van Genuchten, M.T., J.M. Davidson, and P.J. Wierenga, "An Evaluation of Kinetic and Equilibrium Equations for the Prediction of Pesticide Movement Through Porous Media," Soil Soc. Amer. Proc., 38:29-35 (1974).

18. Goltz, M.N., and P.V. Roberts, "Interpreting Organic Solute Transport Data from a Field Experiment Using Physical Nonequilibrium Models," Journal of Contaminant Hydrology, 1:77-93 (1986).

19. U.S. EPA, Methods for Organic Chemical Analysis of Municipal and Industrial Waste Water, EPA-600/4-82-057, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1982.

20. U.S. EPA, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. Second Edition, SW-846, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington D.C., 1982.

21. Schwarzenbach, R.P., and J. Westall, "Transport of Nonpolar Organic Compounds from Surface Water to Groundwater," Environmental Science and Technology, 15(11):1360-1367 (1981).

22. Park, K., Degradation and Transformation of Polycyclic Aromatic Hydrocarbons in Soil Systems, Ph.D. Dissertation, Department of Civil and Environmental Engineering, Utah State University, Logan, Utah, 1987.

23. U.S. EPA, Permit Guidance Manual of Hazardous Waste Land Treatment Demonstrations. EPA-530/SW-86-032, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington D.C., 1986.

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